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UV−vis and IR Spectral Characterization of Persistent Carbenium Ions, Generated upon Incorporation of Cinnamyl Alcohols in the Acid Zeolites HZSM-5 and HMor

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Cinnamyl alcohol (**1**) and two derivatives **2** and **3** have been incorporated in dehydrated HMor and HZSM-5 zeolites with the aim to characterize spectroscopically the corresponding carbocations generated within the solids. Product studies of the supernatant liquid phase combined with diffuse reflectance UV−vis and IR spectroscopy provide unequivocal evidence for the carbocations. Thus, cinnamyl alcohol (**1**) affords the 1,5-diphenylpentadienyl cation in HMor and HZSM-5 as a persistent species. In the case of HMor with larger pore dimensions the bulkier 1-(2′-cinnamyl)-3-phenylpropenyl cation was also spectroscopically detected. No persistent carbocation was observed when the α-methylcinnamyl alcohol (**2**) was incorporated in the acid zeolites, wherein a complete cyclization to 2-methylindene takes place. Finally, incorporation of 2-methyl-4-tolyl-3-buten-2-ol (**3**) in HZSM-5 allowed detection of the *gem*-dimethyl-subsituted *p*-methylcinnamyl cation, with a lifetime of hours. This cation is not persistent enough in HMor to be characterized. The present study illustrates how structurally related allylic substrates may give distinct carbenium ions whose persistence depends on the host−guest fit in the interior of the acid zeolites.

Introduction

Generation and characterization of carbenium ions inside zeolites has attracted renewed attention in recent years.[1−11] This interest arises from two different points of view: first, zeolites are a convenient heterogeneous medium to stabilize and protect elusive positively charged reaction intermediates such as carbenium ions and radical cations, which allows their spectroscopic characterization and study of their chemical reactivity;[12] and second, generation of persistent carbenium ions has made possible the calibration of the acid strength of the H^+ form of zeolites, a pertinent property since zeolites are the most used solid acids for catalytic hydrocarbon cracking.[13−15] The leading idea behind the latter studies is that the reactivity and persistence of carbenium ions is related to the acid strength of the medium. By attempting the generation of a series of carbocations of different thermodynamic stability, it has been possible to correlate the acid strength of solid acids with that of homogeneous mixtures of acids and superacids. The quintessence of this research is that the strongest acidic zeolites compare either to the acidity of a 70% aqueous solution of sulfuric acid[13] or to pure sulfuric acid;[15] thus, zeolites cannot be considered as superacid solids.

The previous studies on the acid strength of zeolites have not paid attention to the fact that geometrical factors can also contribute to the stabilization of embedded carbenium ions. Thus, when one deals with microporous solids with definitely restricted reaction cavities, besides the intrinsic nucleophilicity of the framework, spatial considerations have to be taken into account.[11,12] Of particular importance are the geometrical restrictions imposed on the approaching external nucleophiles to the carbocationic center such that an effective overlap between the HOMO of the nucleophile and the LUMO on the carbenium ion center can occur. When the transition states or products are larger in size than the available space provided by the pores, the rigid zeolite framework may impede the reaction for steric reasons.[16]

While attempts to generate the parent allyl cation upon inclusion of allyl alcohol in pentasil zeolites have met with failure,[17−19] we have shown that capped α,ω-diphenyl allylic cations persist inside monodirectional mordenite

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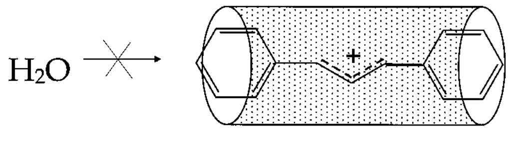
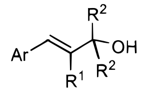


Figure 1. Pictorial representation of the impeded attack of water on the allylic functionality of the α,ω-diphenylpropenyl cation included inside the zeolite channel, whose dimensions closely match that of a phenyl ring.

Chart 1



substrate	Ar	R^1	R^2
1	Ph	H	H
2	Ph	CH_3	H
3	*p*-CH_3-C_6H_4	H	CH_3

and medium-pore ZSM-5 by protection from the attack by external nucleophiles.[20,21] In the case of the 1,5-diphenylpentadienylium incorporated in ZSM-5, the cation survives indefinitely even after suspending the solids in water.[21] It was established by Olah and Spear, by working in liquid SO_2, that phenyl substitution on the allylic system produces only a relatively minor extra stabilization of these allylic ions,[22] which in solution may readily undergo intramolecular cyclization to indenyl cations.[23,24] The contrasting persistence of these substituted α,ω-diphenyl allylic cations within zeolites was attributed to spatial constraints imposed by the tight fit of the phenyl substituents inside the zeolite channels of similar dimensions. In these cases, the end-capping phenyl rings act like stoppers in the channel, which on one hand impede the access of external nucleophiles to the inner positive charge of the allyl bridge and on the other hand impose a linear arrangement preventing cyclization (Figure 1).

Herein we present a product study, combined with spectroscopic data that provide evidence that the incorporation of cinnamyl alcohols within medium-pore and monodirectional large-pore, acidic zeolites also give rise to characterizable carbocations. The molecular structures of the cinnamyl alcohols under study here are depicted in Chart 1. All of them encompass a single aryl ring at one of the termini of the allyl cation bridge. These substrates fill the gap between the as yet not observed allyl cation[18,19] and the remarkably long-lived capped α,ω-diphenyl derivatives in pentasil zeolites.[20,21,25]

Results and Discussion

The reaction of cinnamyl alcohol (**1**) with a large excess of aromatic hydrocarbons in the presence of HZSM-5 and HMor zeolites has been reported to form the corresponding Friedel–Crafts alkylation products, presumably through the intermediacy of the 1-phenylpropenylium cation (**1a**).[26–28] However in these studies, no attention was paid to the characterization of this intermediate in the solid. It is known that the cinnamyl cation can only persist as the dominant species in a strongly acidic medium.[29]

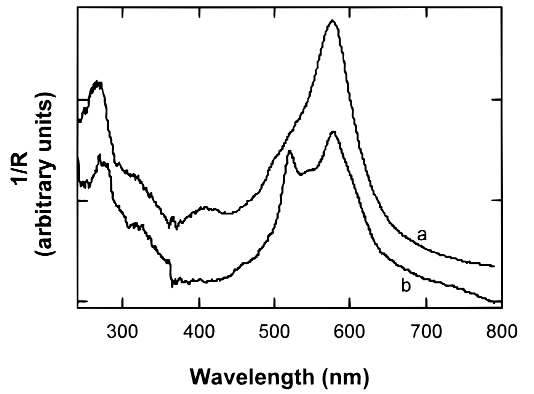


Figure 2. DR UV–vis spectra (plotted as the inverse of the reflectance, *R*) of HZSM-5 (plot a) and HMor (plot b) zeolites after adsorption of the alcohol cinnamyl (**1**).

Incorporation of alcohol **1** inside thermally dehydrated HMor (a parallel channel system of 7.4 Å diameter) or HZSM-5 (two perpendicular channel systems: straight 5.2 × 5.7 Å, sinusoidal 5.3 × 5.6 Å), by stirring at the reflux temperature a solution in CH_2Cl_2 or CCl_4, gave rise to an intense purple coloration of the solid. Diffuse reflectance UV–vis (DR) spectrum of the HZSM-5 zeolite (Figure 2) showed the presence of a new band at 580 nm, with a shoulder at 520 nm. This band is absent in the starting cinnamyl alcohol or any of its simple neutral or charged derivatives. In particular, the cinnamyl cation has an absorption band at 380 nm and, therefore, can be unequivocally ruled out as the species responsible for the purple color of the solid. We noticed that the DR spectrum of HMor has an extra absorption band at 515 nm, which suggests that a second species is present in this zeolite.

Product studies gave an important clue on the nature of the intermediate formed upon incorporation of substrate **1** in the zeolites. Solid–liquid extraction allowed recovery, together with unreacted alcohol **1**, of 1,5-diphenyl-1,4-pentadiene (**4**) and 2-cinnamylindene (**5**). The structure of both compounds was confirmed by comparison with authentic samples, obtained by alternative synthesis as indicated in the Experimental Section. The **4**:**5** product ratio in the organic phase changed from 60:40 for HMor to 20:80 for HZSM-5. The variation in the **4**:**5** ratio indicates that the dimensions of the zeolite micropores play a role in the product distribution found in the liquid phase and presumably also in the material retained inside the voids. In this regard, molecular modeling at the semiempirical level has indicated that indene derivative **5** is too bulky to fit inside the ZSM-5 pores. Therefore, this product is formed presumably on the external surface of the ZSM-5 particles, but not in their interior.

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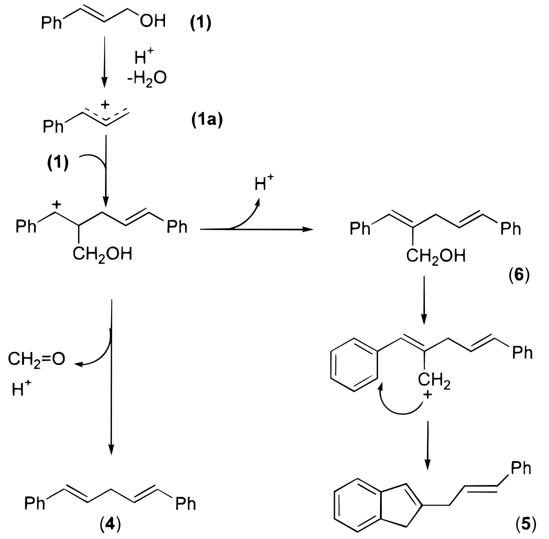
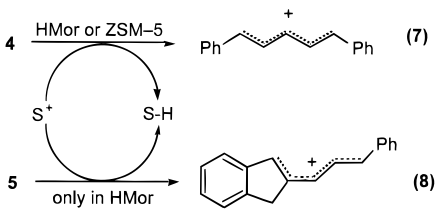
Scheme 1



Scheme 2



The formation of the indene product **5** may be readily understood as arising from the intramolecular cyclization of an intermediary 2-hydroxymethyl-1,5-diphenyl-1,4-pentadiene (**6**), the dimer that arises from the electrophilic attack of a cinnamyl cation on the C═C bond of the cinnamyl alcohol (**1**) as shown in Scheme 1. Alternatively, the same dimer **6** could be formed through a concerted acid-catalyzed mechanism in which cinnamyl cation (**1a**) is not fully developed. This would agree better with the lower acid strength of the zeolites compared to superacid media and with the previous failure to generate the parent allyl cation in ZSM-5.[18,19] Although the mechanism of formation of diene **4** is uncertain at the moment, there are precedents in the literature in which arylalkenes such as **4** are formed by acid-catalyzed cleavage of methylols.[30,31] This provides support that the diene **4** and its precursor **6** are generated upon incorporation of the cinnamyl alcohol (**1**) in the acid zeolites with the cinnamyl cation (**1a**) as the primary common intermediate (Scheme 1).

With the presence of diene **4** in the organic phase established, the most likely species responsible for the purple color in the acid zeolites should be 1,5-diphenylpentadienylium cation (**7**), formed from diene **4** through hydride abstraction (Scheme 2). The hydride acceptor could be any other more reactive carbenium ion. The DR spectrum of HZSM-5 perfectly matches that previously reported by us for the cation **7** in the same zeolite.[20,21]

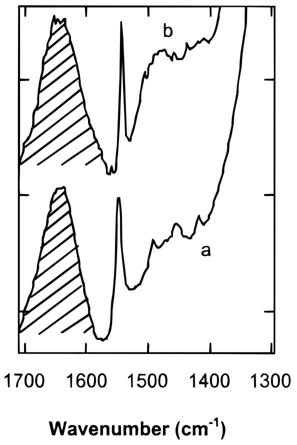


Figure 3. Aromatic region of the IR spectra of two HZSM-5 wafers in sealed cells after degassing at 200 °C for 1 h under 10^{-2} Pa, recorded at room temperature: (a) after incorporation of 1,5-diphenyl-1,5-diacetoxypentane as described in ref 20, and (b) after reaction of cinnamyl alcohol (**1**) at reflux of CH_2Cl_2. Spectrum a corresponds to the α,ω-diphenyl allylic cation **7**; the shaded band corresponds to an overtone of the aluminosilicate framework.

Unambiguous confirmation of the assignment for the purple species as pentadienylium cation **7** was obtained by IR spectroscopy. The spectral window, in which the zeolite framework is transparent for IR spectroscopy (3300−1300 cm^{-1}), has been found useful to characterize the organic species embedded within zeolite matrixes.[12,32] Indeed such spectroscopy serves as a fingerprint, in which a good match between the IR spectrum of the embedded organic guest and of the same species in another medium is considered as one of the safest criteria for identification. IR spectroscopy can also be used to rule out a charge-transfer complex between diphenylpentadiene and the zeolite as responsible for the 580 nm band in the DR spectra.

In the case considered here, the IR spectrum of cation **7** in the HMor zeolite had been already reported.[20] As it can be seen in Figure 3, the spectra of the zeolite wafers after incorporation of cinnamyl alcohol (**1**) coincide with that of carbenium ion **7**, and therefore, on the basis of the DR UV−vis and IR spectra, we may conclude that they are the same species.

As mentioned earlier, the DR spectrum of HMor does not coincide exactly with that of cation **7**, because a second species may also be present. On the basis of the reaction products, we speculate that the indene derivative **5** could also serve as the precursor for the stabilized carbenium ion **8** by hydride abstraction (Scheme 2). The alternative hydride abstraction of an indenyl hydride to afford the benzocyclopentenyl cation seems unlikely in view of the 4π-antiaromatic nature of the latter. In fact, the incorporation of the authentic indene **5** in HMor gives rise to the DR spectrum shown in Figure 4, characterized by two unresolved bands with λ_{max} at 515 and 580 nm. Thus, the 515 nm band in this spectrum corresponds to the allyl cation **8**, generated from indene **5** through hydride abstraction (Scheme 2). Comparison of Figures 2 and 4 manifests that the DR spectra of HMor with the incorporated alcohol **1** is a superposition of individual spectra corresponding to the cations **7** and **8**.

The DR shown in Figure 2 does not exhibit any significant decay in the intensity of the 580 nm band over days. Thermogravimetric analysis of these ZSM-5 and HMor samples incorporating cation **7** and **8** show the presence of ca. 8 wt % of coadsorbed water simulta-

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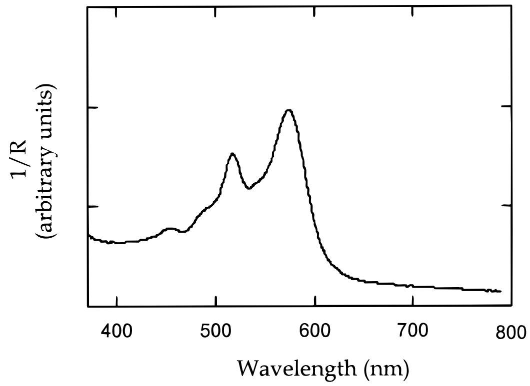


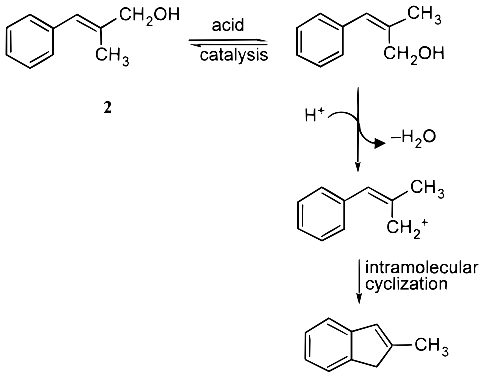
Figure 4. DR spectrum of a HMor sample after incorporation of the indene derivative **5**.

neously with these carbocations. The amount coadsorbed is less than that adsorbed on the original zeolites prior to the adsorption (over 15%). This reflects a certain hydrophobization of the zeolite by incorporation of the organic material, but the residual amount of water is still high enougth to quench totally any cation in solution. Thus, a reasonable explanation to justify how simultaneously water and cations **7** and **8** can coexist is based on the steric constraints imposed by the lattice to the attachment of water on the positive carbocation center as depicted in Figure 1.

Unfortunately, the authentic cation **8** could not be generated inside the ZSM-5 zeolite from the indene **5**, because this compound is too large to penetrate into the interior of the pores. The fact that the cation **8** is also not detected inside the medium-pore ZSM-5 zeolite when the cinnamyl alcohol (**1**) is incorporated may be understood on the basis of shape selectivity.[33-35] Compared to large-pore sized Mor (7.4 Å), the ZSM-5 channels (~ 5.5 Å) rigidly hold the linear diene **4** or its derived cation **7** in an extended conformation, which precludes the conformational folding necessary for intramolecular cyclization. This interpretation is in agreement with the very weak and not persistent coloration observed in a control experiment in which the authentic indene derivative **5** was exposed to the ZSM-5 zeolite and also in agreement with molecular modeling calculations. In contrast, indene **5** does diffuse inside the larger channels of Mor and therewith serves as the precursor of the cation **8** (see Figure 4).

To generalize the rather surprising behavior of the cinnamyl alcohol (**1**) upon incorporation into acid zeolites, the related allylic alcohol α-methylcinnamyl alcohol (**2**) was also examined in HMor and HZSM-5. In this case, the observed chemistry was notably different from that of the cinnamyl alcohol (**1**), which helped to clarify the importance of the C═C bond configuration. Thus, incorporation of alcohol **2** into the HMor and HZSM-5 zeolites resulted in 2-methylindene as the only detectable product. No persistent carbocationic intermediate could be observed in the solid, as judged by the absence of any optical absorption at wavelengths longer than 350 nm. This result implies that the immediate carbocation precursor of the 2-methylindene possesses a *cis*-configured C═C bond predestined for intramolecular cyclization, a process that is favored in substrate **2** compared to the intermolecular trapping required for the cinnamyl alcohol (**1**). Thus, the *E*-configured α-methylcinnamyl alcohol (**2**) first undergoes acid-catalyzed *cis*−*trans* isomerization to provide a stationary concentration of *Z*-**2**, which subsequently intramolecularly cyclizes to the indene derivative (Scheme 3). In this regard, GC−MS of the supernatant liquid allowed detection of a minor peak (<5%) during the incorporation process with a MS spectrum identical to that of *E*-**2** that may be attributed to its *Z* isomer.

Scheme 3



The influence of the substituents on the allyl lateral chain and the pore size of the acid zeolite on the persistence of allylic cations is nicely exemplified in the case of cinnamyl alcohol **3**. Geminal dimethyl substitution increases the steric encumbrance at one of the termini of the allyl system and, as suggested by Figure 1, should exert spatial restrictions toward the approach of nucleophiles onto the positive allylic core. At the same time, dimethyl substitution intrinsically stabilizes the resulting allylic carbocation. These two factors should favor the persistence of the *gem*-dimethyl cinnamyl cation derived from substrate **3** with respect to that of the parent cinnamyl alcohol (**1**). The question is, then, whether *gem*-dimethyl subtitution could have the same steric effect as a phenyl cap inside the channels of zeolites.

Indeed, upon incorporation of alcohol **3** in HZSM-5 the zeolite develops a yellow color. The DR spectrum showed an intense sharp band at 430 nm, which decays within hours and indicates the generation of the corresponding allyl cation (Figure 5A). The same optical spectrum was recorded when substrate **3** is dissolved in trifluoroacetic acid, although in this solution the band was hypsochromically shifted by 30 nm (Figure 6).

The 430 nm band is, however, not observed upon incorporation of alcohol **3** in HMor (Figure 5B). In this case, the larger pore size of the mordenite compared to the pentasil zeolites provides a more loosely held 1,1-dimethylcinnamyl cation inside the mordenite channels; thus, this cation may be trapped by coadsorbed water or nucleophilic framework oxygens of HMor. The actual situation is, however, more complex since a weak absorption band is observed at 630 nm for mordenite (see inset of Figure 5B), which decays with time and presumably corresponds to a different carbocation. This band is not observed in the case of ZSM-5. A transient species with such long wavelength absorption may arise from intermolecular dimerization of the substrate **3**, analogous to that shown in Scheme 1 for the cinnamyl alcohol (**1**).

In conclusion, the persistent carbocationic species generated from cinnamyl alcohols by incorporation in acid

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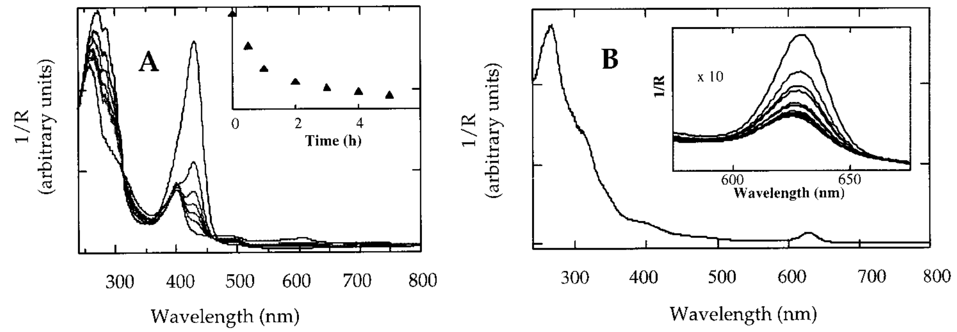

Figure 5. (A) DR spectrum (plotted as the inverse of the reflectance, *R*) of a HZSM-5 sample after incorporation of alcohol **3** from a CH_2Cl_2 solution, recorded at different time intervals; the inset displays the decay of the intensity measured at 390 nm as a function of time. (B) DR UV−vis spectrum of a HMor sample (as in spectrum A); the inset shows the decay of a weak absorption band at 630 nm, probably due to minor amounts of a highly delocalized carbenium ion.

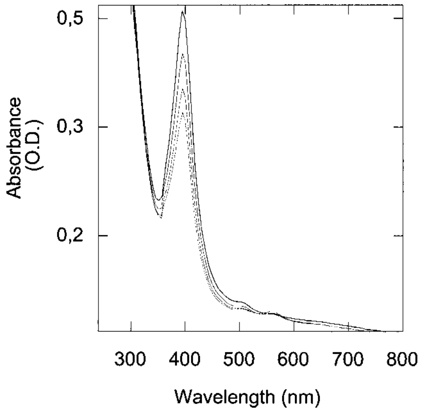

Figure 6. UV−vis absorption spectra of alcohol **3** dissolved in CF_3CO_2H (ca. 10^{-3} M) recorded at 1 h intervals.

zeolites may be observed quite generally. The structure of the carbenium ion depends on the substitution pattern of the cinnamyl alcohol precursor and on the pore dimensions of the zeolite. The chemistry may be rationalized in terms of acid-catalyzed dehydration of the cinnamyl alcohols by the acid sites of the zeolite. When the primary cinnamyl cation is sufficiently bulky to persist in the channels of the zeolite, then such cations may be spectroscopically characterized. An unsubstituted cinnamyl functionality dimerizes or intramolecularly cyclizes to extendedly conjugated cation intermediates. For example, the unprecedented formation of the 1,5-diphenylpentadienylium ion from cinnamyl alcohol has been assessed by UV−vis and IR spectroscopy. Significantly, a *gem*-dimethyl terminus is sufficient to stabilize and protect the initial allylic carbocation within ZSM-5 against bimolecular reactions (although less efficiently than a phenyl cap) but not in the larger channels of the mordenite.

This work is relevant for the use of acid zeolites as heterogeneous catalysts or supramolecular hosts for processes that involve carbenium ion intermediates.

Experimental Section

Cinnamyl alcohols **1** and **2** were commercial samples (Aldrich) and were used as received. 2-Methyl-4-(4-methylphenyl)-3-buten-2-ol (**3**) was prepared by addition of 2 equiv of MeLi at −78 °C to ethyl *p*-methylcinnamate, which was obtained in a Reformatsky reaction from ethyl bromoacetate and 4-methylbenzaldehyde.[37] HMor was obtained by ammonium decomposition at 550 °C under air of a commercial NH_4Mor (P.Q. CBV 20A, Si/Al 14). HZSM-5 was prepared by template decomposition of Et_4N−ZSM-5 by following the reported procedure.[38] The Si/Al ratio of the resulting HZSM-5, measured by chemical analysis, was 27. The incorporations were carried out at reflux temperature by stirring magnetically a suspension of the corresponding cinnamyl alcohol (20 mg) in CH_2Cl_2 or CCl_4 (15 mL) in the presence of thermally dehydrated (500 °C, overnight) zeolite (1.00 g) for 2 h. After this time, the solid was filtered and Soxhlet extracted with CH_2Cl_2. The combined organic phases were analyzed by GC−MS quadrupolar mass spectrometer equipped with a 25 m capillary column of cross-linked 5% phenylmethylsilicone and GC−FTIR gas chromatograph with the same column as the GC−MS and coupled to a FTIR detector. The solvent was then removed under reduced pressure, and the residue was purified by thin-layer chromatography with mixtures of hexanes−CH_2Cl_2 as eluent. ^1H and ^{13}C NMR spectra of the isolated compounds were recorded on a 300-MHz NMR instrument with $CDCl_3$ as solvent and TMS as internal standard. DR UV−vis spectra of the solids were recorded on a spectrophotometer by using a praying mantis accessory and $BaSO_4$ as calibration standard. FTIR spectra of the zeolites with the organic material were recorded in a spectrophotometer by using a greaseless cell supplied with CaF_2 windows. Self-supported wafers (10 mg) were compressed at 1 ton × cm^{-2}. Prior to recording the IR spectra at room temperature, the samples were successively degassed at room temperature, 100, 200, and 300 °C under 10^{-2} Pa for periods of 1 h.

2-Methylindene was characterized by comparison with a commercial sample (Aldrich). The diene **4** was identified by comparison with an authentic sample, which was obtained by dehydrohalogenation of 1,5-dichloro-1,5-diphenylpentane[39] with sodium carbonate. 2-Cinnamylindene (**5**) was synthesized in 68% from 2-cinnamyl-1-indanone (1.00 g, 4.00 mmol) by $NaBH_4$ (160 mg, 4.00 mmol) reduction in EtOH (10 mL) and subsequent dehydration with phosphoric acid (400 mg). 2-Cinnamyl-1-indanone was obtained in 78% yield by reacting 1-indanone (1.00 g, 7.60 mmol) with NaH (365 mg of a 60% suspension in mineral oil) in dry THF (5 mL) at −10 °C for 2 h and then adding a solution of cinnamyl chloride (1.20 g, 7.60 mmol) in dry THF (5 mL) at room temperature for 5 h.

2-Cinnamylindene (5). ^1H NMR δ (ppm): 7.39−7.11 (m, 9H, Ar−H), 6.6 (s, 1H, H at 1), 6.5 (d, 1H, J = 16 Hz, PhC*H*=CH−), 6.3 (dt, 1H, J_1 = 16 Hz, J_2 = 7 Hz, PhCH=C*H*−), 3.4 (s, 2H, H at 3), 3.3 (d, 2H, J = 7 Hz). ^{13}C NMR δ (ppm): 131.4, 128.5, 127.9, 127.3, 127.2, 126.3, 126.1, 123.8, 123.5, 120.1, 41.1, 34.8. HR−MS (*m/z*): calcd for $C_{18}H_{16}$ 232.1253, found 232.1342.

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